N-Methylation of Wholly Aromatic Polyamides for Size-Exclusion Chromatography

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SYNOPSIS

Wholly aromatic polyamides, including poly(1,4-phenyleneisophthalamide) and poly(1,4-phenyleneterephthalamide) are N-methylated to render them soluble in N,N-dimethylformamide, a common size-exclusion chromatography eluent. The procedure N-methylates 50–55% of the total amide linkages in these two examples, permitting reproducible measurement of their absolute molecular weight distributions using differential viscometry detection. There is no observable degradation in molecular weight resulting from the N-methylation, provided the excess methylating reagent is destroyed shortly after completion of the derivatization by quenching with potassium acetate. The validity of the molecular weight data obtained by the method is confirmed by light-scattering measurements on derivatized polymer and by comparison to the molecular weight of underivatized polymer that can be approximated from the intrinsic viscosity in concentrated sulfuric acid. The method is applicable to a variety of wholly aromatic polyamide structures. Examples are given.

INTRODUCTION

Wholly aromatic polyamides, also referred to as polyaramids, are useful in applications requiring high thermal stability and high moduli. Poly(1,4-phenyleneisophthalamide) (PPIA) and poly(1,4-phenyleneterephthalamide) (PPTA) were two of the first of these materials, commercialized by DuPont as Nomex and Kevlar (polyamides), respectively. They find use as replacements for steel, glass, aluminum, and fiberglass in various capacities because of their light weight, inherent flame resistance, and high tensile strength. Two of the more well-known applications of these materials are personal protection apparel, such as the bulletproof vest and cord material for belted automobile tires. Their unique properties are a result of rigid-rod structure and strong intermolecular hydrogen bonding, both of which also make them difficult to process and characterize. For example, many wholly aromatic poly-amides are soluble mainly in strongly corrosive, protic solvents such as concentrated sulfuric acid, methane sulfonic acid, and chlorosulfonic acid. This has made it particularly difficult to measure molecular weights and molecular weight distributions (MWDs), since most methods require dissolution of the sample. Despite their limited solubility, wholly aromatic polyamides, including PPIA and PPTA, have been characterized in solution (e.g., Refs. 1 and 2 and references therein). MWDs of PPTA have been obtained by photon correlation spectroscopy[3] and size-exclusion chromatography (SEC)[4] in concentrated sulfuric acid. Generally, SEC is the preferred method for measuring MWDs; however, handling and pumping corrosive, acidic eluents make this method less than desirable for most laboratories. In fact, very few applications (e.g., Ref. 5) have appeared in the literature since the original SEC of PPTA in concentrated sulfuric acid by Arpin and Strazielle[4] more than two decades ago. As a result, molecular weights are commonly approximated from a single-point (e.g., inherent) viscosity measurement.

An alternative SEC procedure involving the N-alkylation of PPTA was described more recently.[6] Low-molecular-weight (less than 13,000 polystyrene equivalent molecular weight) samples were made soluble in common solvents such as tetrahydrofuran by formation of the N-propyl derivative. SEC was demonstrated for three derivatized samples of different molecular weights; however, the distributions were reported as polystyrene equivalent molecular weights and the application of universal calibration was not demonstrated. It is also unclear if the method is generally applicable to materials of higher molecular weight. In addition, it requires the use of sodium hydride and extremely dry solvents, which are not desirable to handle in large quantities for routine characterization.

In this paper, we present an N-methylation procedure for wholly aromatic polyamides that solubilizes them in a common SEC solvent, N,N-dimethylformamide (DMF), containing 0.01 N LiNO$_3$. With the use of molecular weight-sensitive SEC detection, we are able to measure absolute molecular weight distributions of these materials quickly and reproducibly and demonstrate that the method can be used routinely and safely on a variety of wholly aromatic polyamides. In addition, the procedure is applicable to related materials such as aromatic polyamideimides that are either insoluble or show anomalous behavior in common SEC solvents.

EXPERIMENTAL

Materials

PPIA (type 450 Nomex staple, 1.5 denier × 2 in. cut-length) and PPTA (Kevlar pulp) were obtained from DuPont, (Wilmington, DE). Other wholly aromatic polyamides and polyamideimides were synthesized in these laboratories. N,N'-Diphenyl terephthalamide (I), a trimeric model for PPTA, was prepared by heating terephthaloyl chloride with aniline in dichloromethane. The white solid was isolated by filtration and triturated in boiling water, acetone, and then methanol. The product was dried under vacuum at 100°C for 18 h. NMR (CDCl$_3$): δ 7.1, t(2H); δ 7.4, t(4H); δ 7.8, d(4H); δ 8.1, s(4H); δ 10.4, s(2H). Assay by titration: 99.9 wt %. N-Phenyl-N-methyl-N'-phenyl-N'-methyl terephthalamide (II), a trimeric model for fully methylated PPTA, was prepared by reacting N-methylaniline and terephthaloyl chloride in the presence of triethylamine at 10°C in dichloromethane. Triethylamine hydrochloride was removed by filtration,

and the dichloromethane solution of the product was extracted successively with dilute HCl, NaHCO$_3$, and NaCl, and dried over MgSO$_4$. The solvent was evaporated to yield an off-white product, which was then dried at 60°C for 72 h.

Elemental analysis—found (expected): C, 76.5% (76.7%); H, 6.0% (5.8%); N, 8.2% (8.1%); O, 9.0% (9.3%); Cl, 0.3% (0.0%). NMR (CDCl$_3$): δ 3.43, s(6H); δ 6.92, d(4H); δ 7.09, s(4H); δ 7.15, q(6H); mp 211–214°C.

All other solvents and reagents were reagent ACS grade obtained from Kodak Laboratory Chemicals, Rochester, NY. They were used without further purification.

Preparation of N-Methyl Derivatives for SEC

The following derivatization procedure is for PPIA or PPTA, with repeat unit equivalent weights of 119 g/eq. A 20–50% stoichiometric excess of base to amide is recommended. We suggest that the amount of base be adjusted appropriately if the equivalent weight of the wholly aromatic polyamide differs significantly from PPIA and PPTA.

To 20–25 mg (0.17–0.21 meq) of wholly aromatic polyamide in 5 mL of DMSO is added 0.25 mL of 1N KOH (0.25 meq) in methanol. A color change is observed (e.g., PPTA, orange; PPIA, yellow), and the solution tests strongly alkaline to moist pH paper. The solution is stirred at room temperature until the sample dissolves (1 h for PPTA, overnight for PPIA). The solution becomes highly viscous as the polymer dissolves. To the solution of soluble polyanion is added 0.05 mL (0.75 meq) of methyl iodide[†] (neat). A slight haze or precipitate of potassium iodide may be observed nearly immediately, and the solution turns pale yellow to nearly colorless within 30 min. The viscosity decreases markedly and the solution now tests slightly acidic to moist pH paper. The solution is stirred for 0.5 h and 70 mg of solid anhydrous potassium acetate is added to quench the excess methyl iodide. The solution is stirred until the potassium acetate dissolves ($\sim$ 3 h), and 15 mL of DMF containing 0.01 N LiNO$_3$ is added. The solution is filtered through a 0.45 μm Teflon filter before SEC analysis.

Isolation of N-Methyl Polyamides

The stoichiometry of the above procedure was followed for 1 g quantities of PPIA and PPTA. The

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[†] Methyl iodide may reasonably be expected to be a human carcinogen. It should be handled accordingly.

N-methylated products were precipitated into a large excess of acetone, isolated by filtration, and dried under vacuum at 50°C for 24 h.

Light Scattering

The refractive index increments of PPIA and PPTA were measured in DMSO at 25.0°C in a KMX-16 differential refractometer (LDC Analytical, Riviera Beach, FL). Absolute light-scattering intensities were measured in DMSO in the static mode at 6–7° from the incident beam in the forward direction using a KMX-6 low-angle laser light-scattering (LALLS) photometer (LDC Analytical). The weight-average molecular weight, $\bar{M}_w$, and second virial coefficient, A_2, were calculated from plots of K/R_θ vs. $1/C$.

Viscometry

The viscosity of PPTA in concentrated sulfuric acid was measured in a Schott Geräte Type II Ubbelohde microdilution viscometer at 25.0°C. No kinetic energy corrections were necessary. Measurements were made in the concentration range of $\eta_{rel} < 1.4$. The data were analyzed by nonlinear regression of the Huggins equation:

$$\eta_{sp} = [\eta]c + k'[\eta]^2c^2 + \cdots \tag{1}$$

neglecting third- and higher-order terms of the virial equation.

NMR

Proton spectra were obtained on a Varian 300 SX spectrometer. Approximately 20 mg of sample were dissolved in 1 mL of deuterated DMSO (Aldrich Chemical Co., Milwaukee, WI) containing 1% tetramethylsilane. Interferring water resonances were shifted away from the *N*-methyl resonances of the products by addition of 5.0 μL of trifluoroacetic acid (TFA) to each solution.

Nonaqueous Titrimetry

Potentiometric titration curves were recorded with a Metrohm model E670 Titroprocessor equipped with a model E665 Dosimat and a 10 mL buret unit. Samples were dissolved in DMSO and titrated with 0.1*N* hexadecyltrimethylammonium hydroxide (HDTMAH) in 9 : 1 (v/v) toluene/methanol. The

titrant was standardized against primary standard grade benzoic acid (Fisher Scientific). Solution potentials were measured using a combination glass/calomel electrode with an internal electrolyte of 0.1*N* tetramethylammonium chloride in methanol.
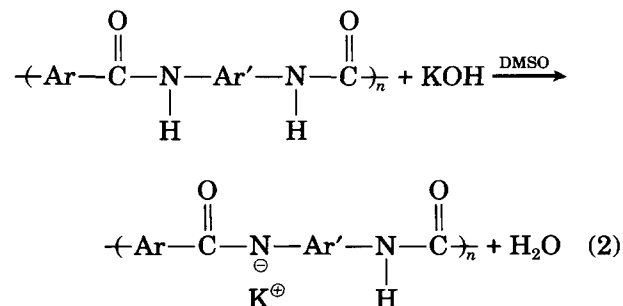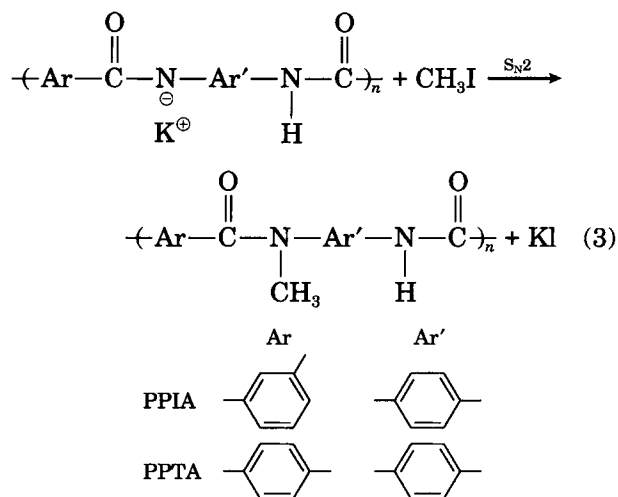
Size-Exclusion Chromatography (SEC)

The SEC system was similar to that described in detail previously.[7] Three HT Linear mixed-bed columns (Waters, Division of Millipore, Milford, MA) and one 30 nm pore-diameter HT column (experimental column provided by Waters), all 8.0 mm i.d. × 300 mm, were coupled in series. The outlet of the column set was connected to a UV detector, after which the flow was split approximately equally between a model 100 differential viscometer (DV) (Viscotek Corporation, Porter, TX) and a Waters model 410 differential refractive index (DRI) detector. The eluent was HPLC-grade DMF containing 0.01 *N* LiNO$_3$. The columns, DV, and DRI were thermostated to 35.0°C. The column set was calibrated with narrow molecular weight distribution poly(methyl methacrylate) standards as described previously.[7] Sample injection volumes were 100 μL, and the flow rate was nominally 1.0 mL/min. The actual flow rate was calculated from the retention volume of a negative system peak at approximately 46 mL using the internal standard method of Patel.[8]

RESULTS

N-Methylation

The *N*-methylation procedure of wholly aromatic polyamides used in this study is an adaptation of well-known analytical derivatization procedures employed previously in the methylation of carboxylic acids.[9-11] It involves the nucleophilic substitution (S_N2) of an alkyl iodide by a soluble polyanion in a highly polar solvent medium:

$$\underset{H}{\underset{|}{+Ar-\overset{O}{\overset{||}{C}}-N}}-Ar'-\underset{H}{\underset{|}{N-\overset{O}{\overset{||}{C}}}}+_n + KOH \xrightarrow{DMSO}$$

$$+Ar-\overset{O}{\overset{||}{C}}-\underset{\overset{\ominus}{K^{\oplus}}}{N}-Ar'-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{||}{C}}+_n + H_2O \tag{2}$$

$$+Ar\!-\!\overset{\overset{\textstyle O}{\|}}{C}\!-\!\underset{\underset{\textstyle K^{\oplus}}{\overset{\ominus}{N}}}{N}\!-\!Ar'\!-\!\underset{\underset{\textstyle H}{|}}{N}\!-\!\overset{\overset{\textstyle O}{\|}}{C}\!\!\underset{n}{\overset{}{)}} + CH_3I \xrightarrow{S_N 2}$$

$$+Ar\!-\!\overset{\overset{\textstyle O}{\|}}{C}\!-\!\underset{\underset{\textstyle CH_3}{|}}{N}\!-\!Ar'\!-\!\underset{\underset{\textstyle H}{|}}{N}\!-\!\overset{\overset{\textstyle O}{\|}}{C}\!\!\underset{n}{\overset{}{)}} + KI \quad (3)$$

	Ar	Ar'
PPIA		
PPTA		

Using this procedure, we obtain $50 \pm 1\%$ (four determinations) and 53% (one determination) N-methylation of PPTA and PPIA, respectively, as determined by ^{1}H-NMR of the isolated products. NMR spectra for the model amide trimer, **I**, the model N-methyl amide trimer, **II**, and N-methylated PPTA are given in Figure 1 (a–c). These spectra indicate that the derivatized PPTA contains unreacted amide groups (δ 10.3, d). We have not investigated the source of two amide proton environments resulting in the doublet at 10.3 ppm seen in Figure 1(c); however, it is not unusual for stereochemistry to result in different proton environments in polymers that are often not observed in related small molecules. N-Alkylation changes the stereochemistry of the amide bond (Ref. 13 and references therein) and both *trans* and *cis* isomers can exist, depending on the degree of N-alkylation.

Quantitative N-alkylation has been reported previously using sodium hydride as the base in reaction 1.[13] Incomplete derivatization of the amide linkages in our procedure can be attributed partially to the use of KOH, a weaker base than sodium hydride, in the formation of the polyanion [eq. (2)]. The two amide linkages of the model amide trimer display distinctly different dissociation constants, as evidenced by the two quantitatively equivalent breaks observed in nonaqueous titration (Fig. 2). The adjacent amide linkages are conjugated through the phenyl rings, which leads to resonance stabilization of the anion. We can postulate that this delocalization of the anion through the stable conjugated system and the high concentration of negative charges on the polyanion chain renders some amide groups too weakly acidic to be deprotonated by hydroxide. Complete derivatization of all amide sites

is not, however, the most important criterion for a viable SEC derivatization procedure. More important are how effectively N-methylation improves the solubility of the aromatic polyamide in SEC solvents and the reproducibility of the SEC results subsequently obtained. As will be shown, both criteria are met with this procedure.

Size-Exclusion Chromatography (SEC)

Examples of the DRI, UV, and DV chromatograms for PPTA are shown in Figure 3. Several peaks in addition to the polymer sample are observed in the DRI and DV detector signals near the total column volume ($\sim$ 44 mL). Some of these peaks are much larger, both in area and height, than the polymer peak. These peaks are caused by excess derivatizing reagents and solvents (DMSO and MeOH), as well as system and gas peaks that are normally observed in DMF/$0.01 M$ LiNO$_3$ SEC separations. The integration window for calculating MWDs only includes signals assignable to polymer (up to 38 mL). The 30 nm pore-diameter column used in addition to the mixed-bed columns improves the resolution of polymer from these low molecular weight peaks, extending the possible integration window for polymer to an elution volume that corresponds to approximately 500 MW, particularly if the UV detector response is used as the concentration sensitive detector.

The intrinsic viscosity of the whole polymer is obtained from the DV detector:

$$[\eta] = \frac{1}{m} \int_0^\infty \eta_{sp}(\nu) \, d\nu \qquad (4)$$

where $\eta_{sp}(\nu)$ is the specific viscosity at retention volume ν, and m is the total mass of polymer injected. The absolute MWD is calculated using a universal calibration curve and the intrinsic viscosity at each retention volume:

$$[\eta](\nu) = \frac{\eta_{sp}(\nu)}{c(\nu)} \qquad (5)$$

where the concentration at each retention volume, $c(\nu)$, is obtained from the DRI detector. In instances where there is interference from solvent and system peaks, there is some advantage to using the UV detector signal to obtain $c(\nu)$. The molecular weight averages and intrinsic viscosities reported in Table
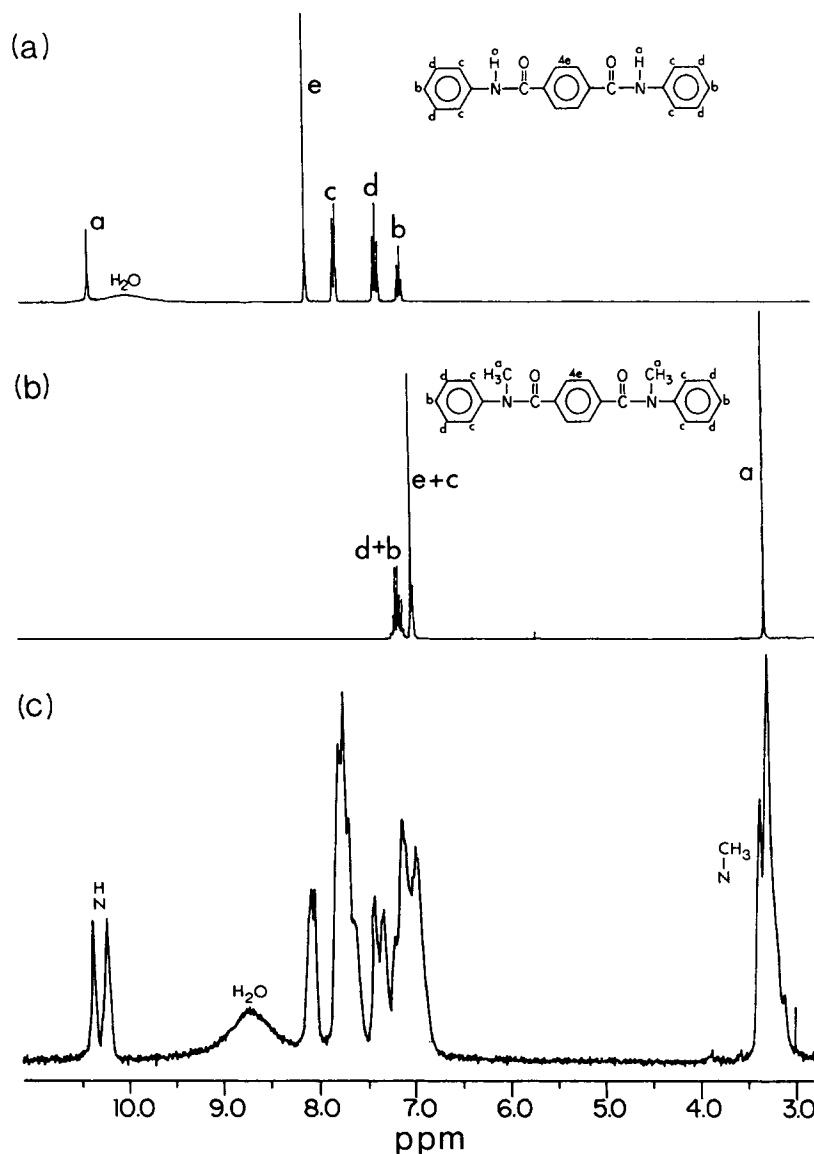
Figure 1 ¹H-NMR spectra of (a) model amide trimer, **I**; (b) N-methyl model amide trimer, **II**; (c) N-methylated PPTA.

I are averages of SEC data obtained from nine independent N-methylations each of PPIA and PPTA, reported with 1 σ standard deviation. This precision is similar to that obtained on this SEC system for a broad molecular weight distribution poly(methyl methacrylate).[7] Also, the weight-average molecular weights calculated from SEC are comparable to those measured by LALLS in the static mode for both polymers (Table I).

The N-methylation procedure results in an SEC sample solution that contains 25% (v/v) DMSO in the DMF/0.01N LiNO₃ eluent. It is generally ad-

visable to inject samples as solutions made up in the SEC eluent to avoid chromatographic artifacts. A co-solvent can selectively solvate the polymer, affecting its hydrodynamic volume, and, in some instances, can cause adsorption of the polymer to the column packing material. No significant differences were observed in the calculated MWDs of PPTA for sample solvents consisting of the DMF/0.01N LiNO₃ containing 5–50% (v/v) DMSO [Fig. 4(a) and (b)]. Concentrations of DMSO > 50% in the sample solvent result in broadened distributions [Fig. 4(c)].
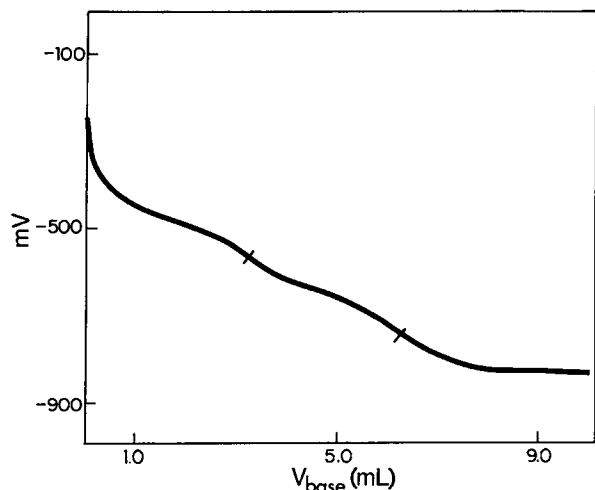
Figure 2   Nonaqueous titration curve of model amide trimer, **I.**

Several workers have measured intrinsic viscosities of PPTA in concentrated sulfuric acid, and the coefficient and exponent for the Mark–Houwink relationship for all of the available data were published recently,[2] $[\eta] = 1.09 \times 10^{-5} M^{1.25}$, where $[\eta]$ is in units of dL/g. Although there is considerable scatter of the available data used to obtain these values, and there is no *a priori* reason to believe that they will apply to our sample of PPTA, we have calculated $M_v \sim 44,000$ from the value of $[\eta]$ for PPTA in H_2SO_4 (Table I). This value is in reasonable agreement with the M_v measured by SEC, which should

be approximately 4% higher than the underivatized polymer molecular weight due to the addition of methyl groups. We cannot state with certainty that there is no degradation of the sample in concentrated sulfuric acid, which may also contribute to the discrepancy between the M_v N-methylated PPTA. It is noteworthy that PPTA is partially protonated in concentrated sulfuric acid and the large value of the exponent α in this solvent is characteristic of a rigid-rod polyelectrolyte.[1]

The coefficient and exponent of the Mark–Houwink equation $[\eta] = KM^{\alpha}$ for N-methylated PPIA and PPTA in DMF/0.01N LiNO₃ obtained from the differential viscometry detector in the SEC experiment are included in Table I. The values are comparable to values for random coil polymers. This is consistent with previous viscosity studies that suggest a random coil structure for N-alkylated PPTA in solution.[12] As explained in Ref. 12, the stereochemistry of the amide bond in rigid PPTA changes from all-*trans* to *trans* with *cis* at the N-alkylated amide groups, which decreases polymer stiffness. Comparison of the absolute MWD to the commonly reported "equivalent" MWD, in our case calculated using poly(methyl methacrylate) standards (Fig. 5), does indicate that the N-methylated PPTA chain is extended in solution compared to other random coil polymers in DMF. The N-methylated PPTA has a molecular size equivalent to PMMA of much higher molecular weight. We have previously reported the values K = 0.000132 dL/g and $\alpha = 0.674$ for PMMA between molecular weights
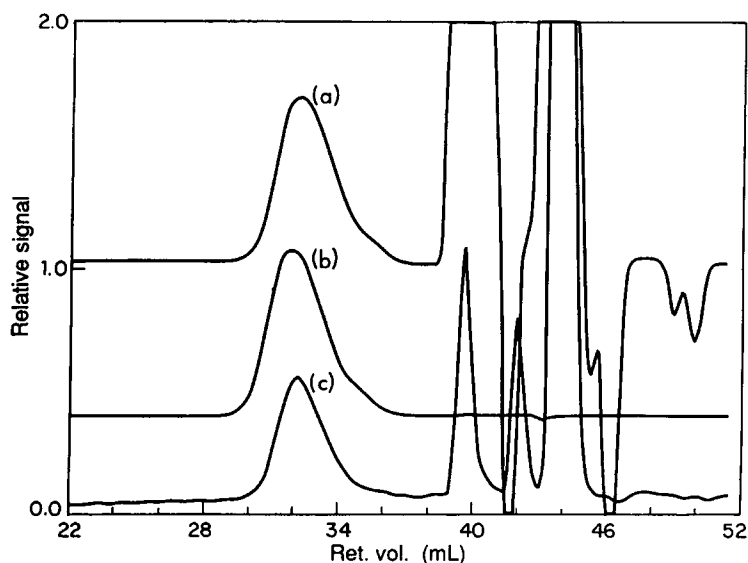

Figure 3   SEC raw chromatograms of PPTA: (a) DRI; (b) UV at 350 nm; (c) DV.

Table I   Characterization Data for PPIA and PPTA

Polyamide	SEC M_n	SEC M_v	SEC M_w	SEC [η] (dL/g)	a^a	log K^a	dn/dc^b	LALLS M_w^b	A_2^a	H_2SO_4 [η] (dL/g)
PPIA	64,000 ± 4000	116,000 ± 3000	110,000 ± 3000	0.53 ± .01	0.74	−4.02	0.147	113,000	5.4 × 10⁻⁴	ND^c
PPTA	27,000 ± 1000	55,000 ± 1000	51,000 ± 1000	0.43 ± .01	0.72	−3.78	0.154	56,000	8.8 × 10⁻⁴	6.94

^{a} DMF/0.01 M LiNO₃, 30.0°C.
^{b} DMSO, 25.0°C.
^{c} Not determined.

10,000 and 1,400,000 in DMF/0.01 M LiBr at 35.0°C.[7] These values can be used with the values of K and α of Table I for PPIA and PPTA to calculate absolute molecular weights via universal calibration, without the use of viscometry detection.

Effects of Reaction Conditions

Previous studies have shown that the use of strong base in the formation of the PPTA polyanion [eq. (2)] does not significantly degrade the solution viscosity of the material[13] (i.e., there is little degradation in molecular weight). To confirm this, a sample was allowed to age in DMSO with KOH for 48 h before addition of methyl iodide. No change in the molecular weight distribution was observed. We have found, however, that allowing the N-methylated polymer solutions to age in the presence of excess methyl iodide can cause substantial decreases

in the absolute MWDs (Fig. 6). The source of this degradation is unknown; however, it is easily prevented by quenching excess methyl iodide shortly after completion of the N-methylation reaction with potassium acetate, which quickly reacts with methyl iodide to form methyl acetate and potassium iodide. Using this approach, we observe no change in the absolute MWD for up to 21 days.

Solubilization of the wholly aromatic polyamide by formation of the polyanion [eq. (2)] is a necessary prerequisite for N-methylation via nucleophilic substitution [eq. (3)]. DMSO is the best general solvent we have found for solubilizing the polyanions of a wide variety of wholly aromatic polyamides. In some instances, DMF is suitable, although certain polymers including PPTA are not solubilized. Potassium hydroxide solubilizes the broadest range of polymer structures in DMSO of any base that we studied. Quaternary ammonium hydroxides (e.g.,
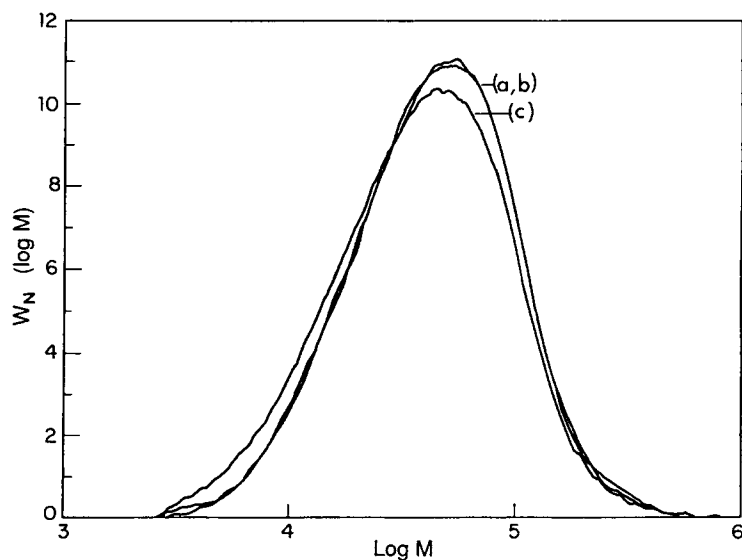

Figure 4   Effects of DMSO concentration in the sample solvent on the calculated MWD:
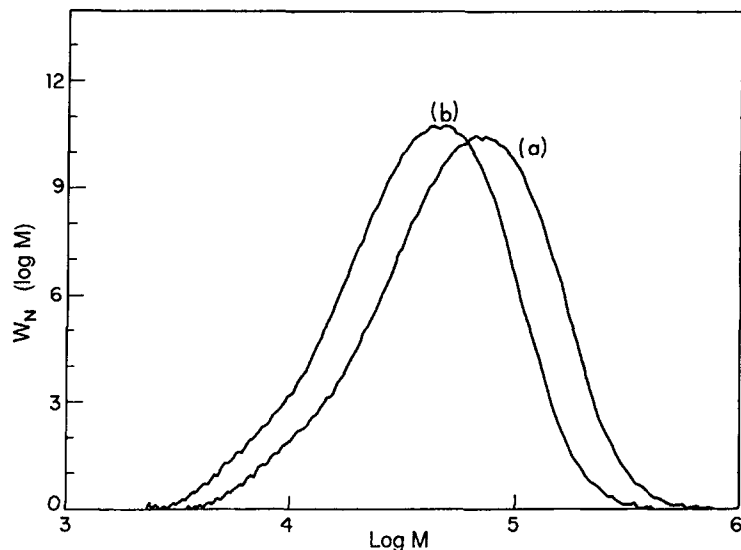(a) 5% (v/v) DMSO; (b) 50% DMSO; (c) 100% DMSO.

Figure 5   Molecular weight distributions of PPTA: (a) PMMA equivalent MWD; (b) absolute MWD.

tetramethyl and tetrabutyl ammonium hydroxides) do not solubilize PPTA in DMSO using the conditions of this study, although it has been shown that there are conditions in which these quaternary ammonium hydroxides will solubilize PPTA.[12] Sodium methoxide dissolves PPTA in DMSO more slowly than KOH, although the subsequent reaction with methyl iodide proceeds normally. We also have noted that a K^+ base counterion is generally better than Na^+ at dissolving the polyanions in DMSO.

All these observations on the solubilization of PPTA polyanions in DMSO are consistent with the results of Burch et al.[14] An excellent, detailed discussion of the solubility and solution properties of the PPTA polyanion is also found in Ref. 14.

The degree of N-methylation is apparently limited by the efficiency of polyanion formation rather than nucleophilic substitution. Heating the sample at 60°C for 2 h after addition of the methyl iodide did not increase the percent methylation. Also, no
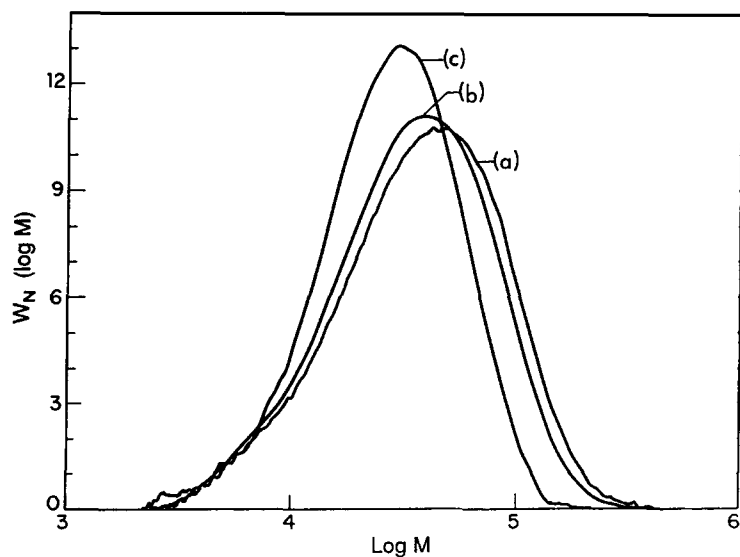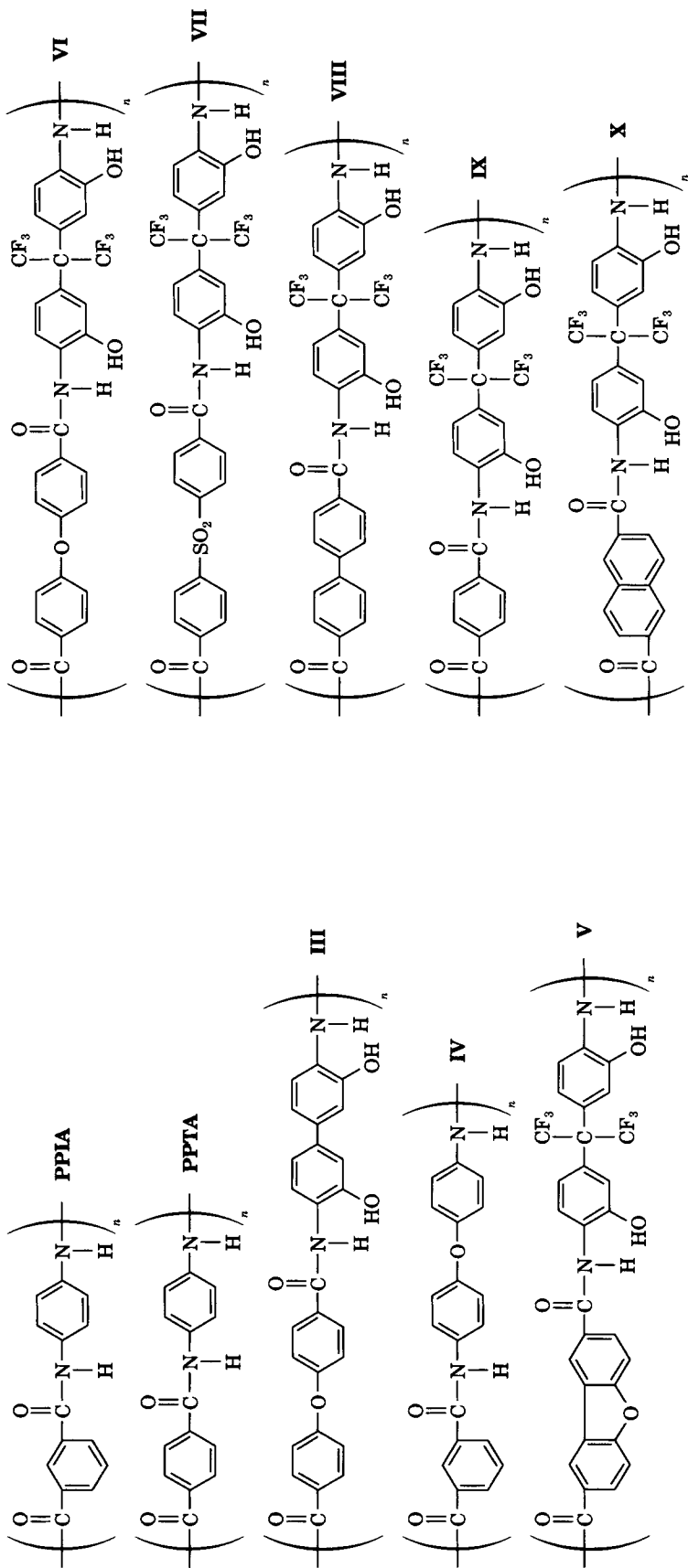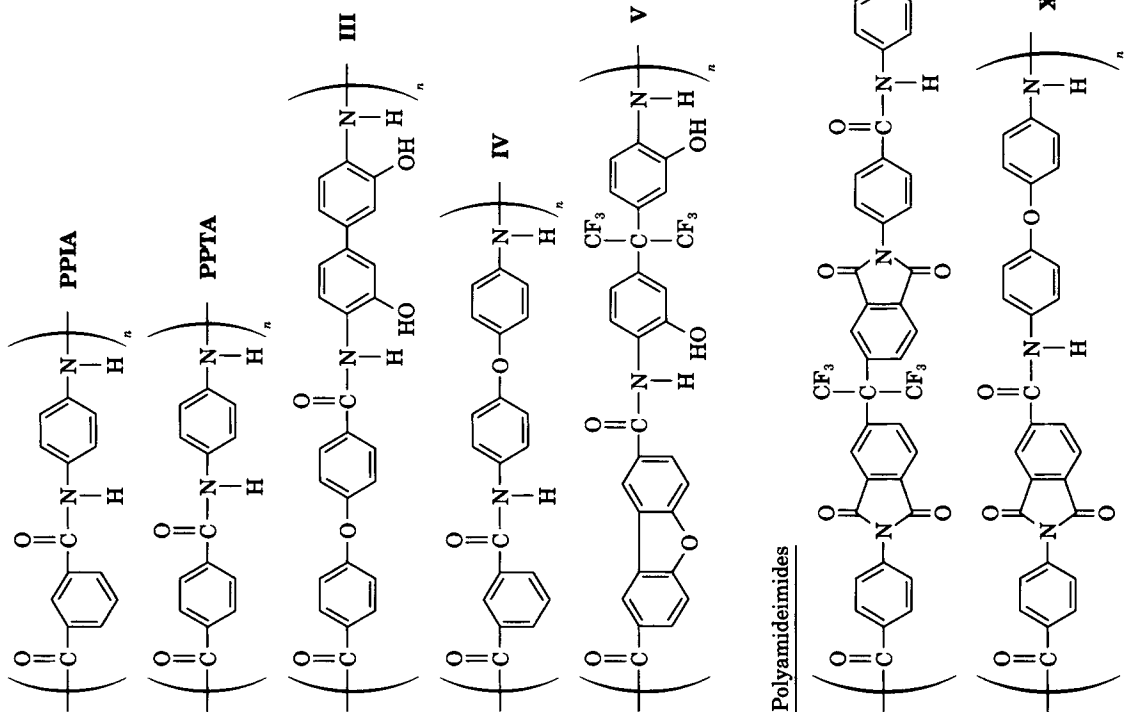

Figure 6   Effects of excess methyl iodide on the MWD of PPTA; reaction not quenched with potassium acetate: (a) 2 h; (b) 48 h; (c) 96 h.
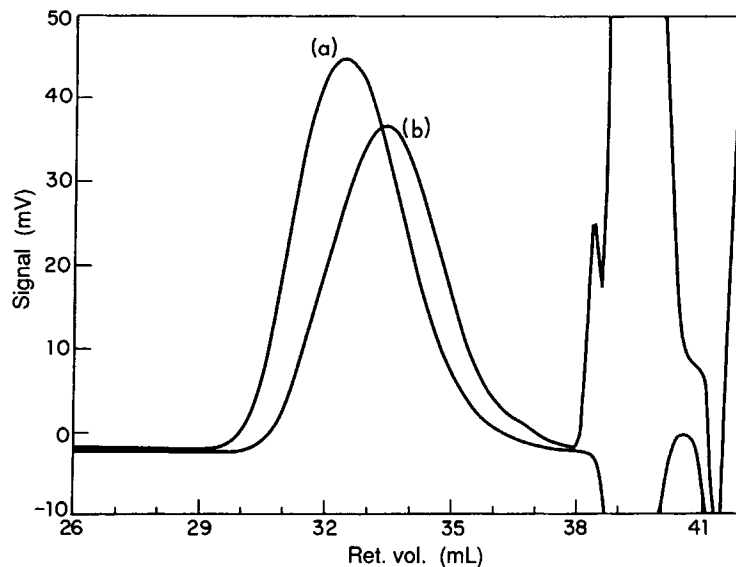
Table II   Molecular Structures of Polyamides

Figure 7 DRI chromatograms of polyamideimide **XI** (a) before and (b) after N-methylation.

improvement in the percent of N-methylation was obtained with a sevenfold stoichiometric excess, rather than a threefold excess, of methyl iodide.

Application to Related Materials

The method is generally applicable to polymers containing wholly aromatic polyamide linkages, e.g., polymers that have aromatic substituents Ar and Ar' in eq. (2). It is not applicable to aliphatic polyamides (e.g., nylon polyamides) or mixed aliphatic-aromatic polyamides. The amide protons of aliphatic materials are not sufficiently acidic to be removed by KOH in DMSO. Also of note is that the procedure does not solubilize oriented PPTA fibers, presumably because of their high degree of crystallinity.

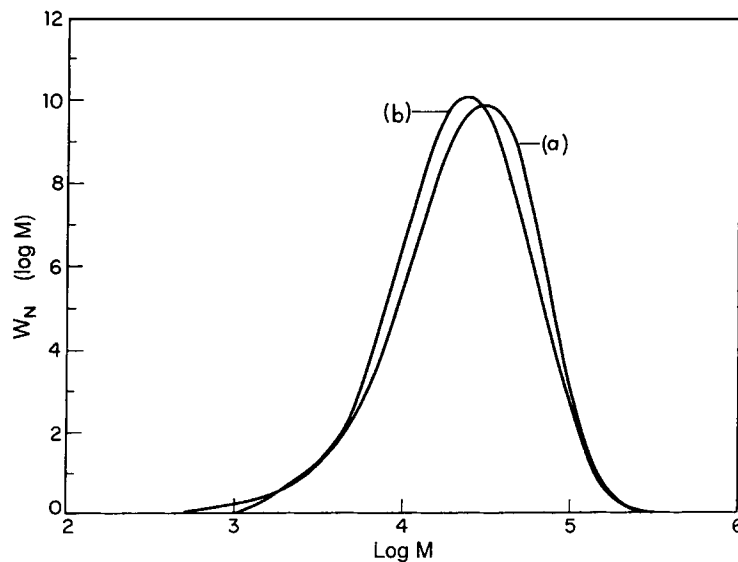Included in Table II is a selection of aromatic polyamides and polyamideimides to which we have

Figure 8 Absolute molecular weight distribution of polyamideimide **XI** (a) before and (b) after N-methylation.
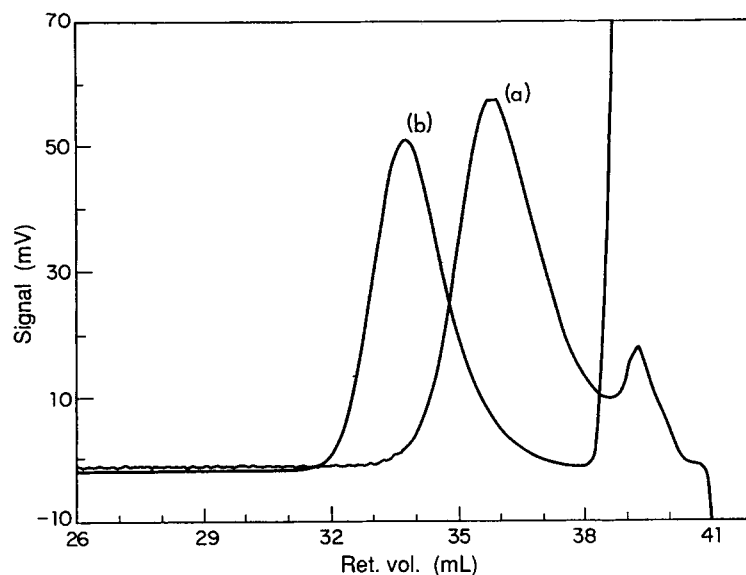
Figure 9 DRI chromatograms of polyamide **VI** (a) before and (b) after N-methylation.

successfully applied this technique. N-methylation of these materials may result in varying amounts of methyl group incorporation; however, in all instances, we obtain reproducible SEC results. Polyamideimide XI (Table II) is soluble in DMF/ $0.01N$ LiNO$_3$ without N-methylation and offers a unique opportunity to examine polymer size before and after derivatization. In Figure 7, it is seen that the hydrodynamic size of the underivatized polymer is much larger than the N-methyl analog; again, this is consistent with a decrease in chain stiffness with N-alkylation and an accompanying decrease in hydrodynamic size, as observed in PPTA.[12] As expected, however, the absolute MWDs of the polymer before and after N-methylation are similar (Fig. 8), and the weight-average molecular weights are nearly identical (31,300 vs. 33,700). N-methylation adds slightly to the molecular weight of the polymer, introducing some uncertainty into the concentration of polymer sample injected. We have made no correction for this, and a slight error in the calculation of intrinsic viscosities and the corresponding molecular weights could account for some of the differences between the two curves. Overall, however, the agreement is sufficiently high to again indicate that there are no deleterious effects on the MWD of these materials with N-methylation.

Some of the polymers listed in Table II are soluble in DMF but exhibit anomalous SEC behavior without N-methylation, including aggregation and adsorption to the SEC column material. Raw chromatograms of polyamide VI (Fig. 9) indicate that

N-methylation effectively eliminates adsorption in this example. It is of note that in most instances phenolic groups will also be methylated, which may also reduce adsorptive effects.

CONCLUSIONS

N-methylation of fully aromatic polyamides is a comparatively simple and safe procedure for the SEC characterization of materials that are normally insoluble in common SEC eluents. As demonstrated in this study, N-methylation also permits spectroscopic characterization of these materials in solution. By minimizing the amounts of the hazardous methylating agent (methyl iodide), and by observing proper precautions for use of toxic SEC eluents such as DMF, we find this procedure to be an effective and safer alternative to performing SEC using corrosive solvents such as concentrated sulfuric acid. Partial N-methylation produces soluble materials and permits reproducible and accurate measurement of molecular weight distributions of materials that have traditionally been intractable for many SEC laboratories.

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